GUIDELINES FOR THE REMEDIATION AND DISPOSAL OF SULPHUR CONTAMINATED SOLID WASTES

Alberta ENVIRONMENT

May 1996

Chemicals Assessment and Management Division
Environmental Regulatory Service

ISBN: 0-7785-0819-6
Pub No.: T/478

Additional copies may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Great West Life Building
9920 –108 Street
Edmonton, Alberta T5K 2M4
Phone: (780) 944-0313
Fax: (780) 427-4407

1 Introduction

Procedures for remediation of sulphur contaminated solid wastes are required to prevent localized soil and groundwater degradation. Careless disposal of these wastes can result in severe soil acidification and contamination of groundwater with acid-leached geoconstituents such as plant nutrients and metals.

Sulphur contaminated wastes originate primarily from the sour gas sweetening industry and occasionally from accidental spills of sulphur during transport to market. Sour gas sweetening with iron sponge or ironite slurry produces a waste product containing pyrite (FeS_2), troilite (FeS), and elemental sulphur (S). A similar process, based on sweetening sour gas with an inorganic zinc compound, generates zinc sulphide. The modified Claus sulphur recovery process is used extensively in Alberta to recover sulphur from sour gas. the process involves oxidizing one third of incoming H_2S to SO_2 and then reacting these two gases over a catalyst to form elemental sulphur. The spent catalyst from this process contains sulphates, sulphides, and elemental sulphur. In addition, sulphur recovery plants produce wastes as a result of spills and operations associated with sulphur storage and handling; wastes from this type of activity include sulphur contaminated soil and filter cakes.

This guideline will assist waste generators, landfill operators, and other people handling sulphur contaminated solid wastes to deal with these materials in an environmentally acceptable manner. Sulphur use, rather than burial, and soil contamination prevention and control need to be given priority, both in the use of this guide and prevention of future contamination.

2 Effects of Sulphur on Soil

Under aerobic soil conditions, the application of sulphur to soil results in the oxidation of sulphur to sulphate. That transformation is largely carried out through oxidizing bacteria which induce the following reaction:

$$S + 3/2\,O_2 + H_2O \rightarrow H_2SO_4$$

Sulphuric acid in the soil solution causes lower pH, increased acidity, higher soluble sulphate content, and reduced microorganism activity. Ion exchange and leaching because of increased acidity result in reduced concentrations of calcium and other basic ions, increased concentrations of phytotoxic ions (Al, Mn), reduced availability of major nutrients such as phosphorus, and greater contribution of nutrients and potentially hazardous ions to surface water and groundwater. To mitigate these effects, a neutralizing agent such as limestone, hydrated lime, or quick lime should be used. When sulphuric acid and these agents are mixed, acid is neutralized and calcium sulphate (gypsum) is produced according to the following reactions:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O$$
$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$
$$H_2SO_4 + CaO \rightarrow CaSO_4 + H_2O$$

Gypsum is only slightly soluble in water and soil salinity problems are unlikely to occur. However, limestone can also contain magnesium carbonate, which will dissolve in the acidic environment produced during sulphur oxidation. The acid neutralization reaction products would then include magnesium sulphate which is much more soluble that gypsum and can cause soil productivity and groundwater contamination problems because of increased salinity. Therefore, a limestone product that is used to neutralize the acidifying effects of sulphur oxidation should contain no more than about 2 % magnesium.

3 Remediation and Disposal Methods

Alberta Environmental Protection encourages solid sulphur waste generators and handlers to consider how wastes might be reduced, recovered, and reused. The use/disposal plan chosen to manage waste materials must ensure environmental protection, accommodate human health needs, and make the best practicable use of sulphur. Recovery of sulphur should be the primary concern for dealing with waste material; *in situ* land surface treatment and land application should be used whenever possible; and landfilling should be used only as a last resort or if other options are inappropriate for the particular waste.

Soils or wastes that contain more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S) are not suitable for *in situ* land surface treatment; the total sulphur content of such materials should be reduced to no more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S) before *in situ* land surface treatment options are considered. Sulphur collected from these cleanup activities must be removed from the contaminated site for recovery or proper disposal. On-site dilution of contaminated material to reduce sulphur content is not allowed.

Land application, on-site pit burial, and landfilling are acceptable disposal methods for soil containing more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S) providing degradative environmental impact is prevented. If land application or on-site pit burial is used, the proponent must submit documentation that demonstrates effective remediation and prevention of degradative environmental impact.

If a soil contains more than 500 $\mu g\ S\ g^{-1}$ (0.05 % S) and no more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S), it can be left in place; the *in situ* land surface treatment process would include addition and incorporation of lime. Waste treatment with lime is not needed providing the total sulphur content is no more than 500 $\mu g\ S\ g^{-1}$ (0.05 % S) and soil pH (2:1 0.01 M $CaCl_2$:soil) is at least 6.5. Documentation supporting effective remediation is required.

Landfilling is required for wastes such as spent catalysts, which contain metals that can become environmentally hazardous if improperly handled.

Acid neutralizing agents suitable for use in sulphur waste treatment include limestone (a mixture of calcium and magnesium carbonates), hydrated lime (calcium hydroxide), and quick lime (calcium oxide). Limestone is useful for *in situ* land surface treatment, land application, landfilling, and on-site pit burial. Hydrated lime and quick lime are suitable for landfilling and on-site pit burial but should not be used for *in situ* land surface treatment or land application because they can raise soil pH above optimum agricultural and forestry production levels. Use of the term "limestone" in the rest of this guide is meant to include these three acid neutralizing agents. Other acid neutralizing agents that can raise soil pH above optimum agricultural or forestry production levels or cause degradation of soil structure, such as sodium hydroxide, should not be used in a sulphur wastes management program.

A sulphur basepad cleanup is used here to illustrate the intent of this guide. Sulphur should be removed from the basepad so that the remaining basepad material contains no more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S). The material removed from the basepad will probably contain some soil or gravel; the sulphur should be reclaimed from this material. If any of the waste materials remaining after sulphur reclamation (including soil, gravel, sulphurcrete/carsul, or any other sulphur contaminated solid wastes) contains no more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S), it can be spread back onto the basepad area. The area should then be treated with lime as outlined in section 3.1 of this guide. If any of the waste materials remaining after sulphur reclamation contains more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S), it can be ground and spread on agricultural land as outlined in section 3.2 of the guide (wastes that contain compounds other than sulphur that pose an environmental risk may require special consideration). The remaining waste material could also be buried in an approved landfill or, with the appropriate approvals, in an on-site pit. Landfilling or on-site pit burial will require lime addition and environmental impact monitoring as described in section 3.3 of this guide.

3.1 Land Surface Treatment

In situ land surface treatment refers to treatment of the material that remains after removing sulphur from, for example, basepad material or the area of an accidental spill. Sulphur must be removed from the material so that no more than 40 000 $\mu g\ S\ g^{-1}$ (4 % S) remains. Limestone must be applied to the remaining material at a rate 3.2 times the weight of sulphur contained in the material and incorporated to the depth of contamination. The limestone used for this purpose should be ground finely enough that at least 90 % by weight passes a 60 mesh sieve.

3.2 Land Application

Land application refers to applying sulphur contaminated (but otherwise non-contaminated) solid waste uniformly to an area of off-site, agricultural land at a maximum rate of 250 kilograms elemental sulphur per hectare. To ensure relatively rapid oxidation of sulphur and

crop benefit, sulphur particle size should not exceed 2 mm (0.08 in). Limestone must be added to receiving soils having a pH less than 6.5 (measured in a 1:2 equilibrated slurry of soil in 0.01 M $CaCl_2$) at a rate of 3.2 times the weight of sulphur contained in the waste. The limestone used for this purpose should be ground finely enough so that at least 90 % by weight passes a 60 mesh sieve. The sulphur contaminated waste, and limestone if needed, should be incorporated into the surface 15 cm (6 in) of soil immediately after spreading. Agricultural land may be used for more than one application of sulphur contaminated waste; however, the waste should not be applied to land until previously applied sulphur has been oxidized. Limestone application, if needed, and cultivation to incorporate limestone and waste into soil should accompany each application of waste.

A soil monitoring program should be used to monitor sulphur oxidation and pH control for land which will receive more than one sulphur application. Soil samples should be taken from representative areas of the treated field and, at each sampling site, from at least the 0 to 15 and 15 to 30 cm depths. If needed, such as for salt impact assessment, samples should also be collected from the 30 to 45, 45 to 60, 60 to 90, 90 to 120, and 120 to 150 cm depths, and if needed to assess further impact, in 50 cm depth increments thereafter. For better data, composite soil samples of at least three separate samples from similar and representative land areas can be made. Soil analyses should include at least pH (measured in 1:2 slurry of soil in 0.01 M $CaCl_2$), elemental sulphur, total sulphur, $CaCO_3$ equivalent, and electrical conductivity. Sulphur contaminated solid wastes should not be applied to land when the ground is snow covered or frozen or at any other time when conditions preclude good application and incorporation control. Land management must ensure the waste is retained on the spread area.

3.3 Landfilling and On-site Pit Burial

Landfilling (at an approved landfill) and on-site pit burial are applicable to all sulphur contaminated wastes, but should be used only as a last option. The primary objectives are to limit the rate of sulphur oxidation, to neutralize sulphuric acid, and to control leaching of the pit contents.

The method consists of excavating a suitably sized pit that is above the water table and in an area underlain by fine-textured materials. Preparation of a pit to receive sulphur contaminated wastes must include lining the bottom and sides of the pit with limestone. Finely ground limestone is preferred to coarser products because of its superior acid neutralizing efficiency, but site management problems, such as trafficability and dusting with high winds, may preclude using a finely ground limestone product. Sieve analysis of a product, known as "3/8's minus", showed that 20 % of the product passes a 60 mesh sieve, 60 % passes a 10 mesh sieve, and 100 % passes a 3/8" sieve. A laboratory investigation which involved leaching a solution of sulphuric acid through columns of this limestone product indicated that a considerable margin of safety is provided as long as a significant content of fine particles is present. Removing the particles which pass a 60 mesh sieve significantly increased the percolation rate and jeopardized

pH control. Limestone products that are used as acid neutralizing agents in landfills and on-site pits should be no coarser than the commercially available product "3/8's minus"; that is, the product should have a particle size distribution such that no less than 60 % of the total weight of the product passes a 10 mesh sieve and no less than 20 % passes a 60 mesh sieve.

The objective in lining a pit for landfilling or for on-site pit burial is to provide a margin of safety against acidic components leaching downward; a layer of limestone at least 50 cm thick should provide such a margin of safety. Limestone should then be added and mixed with the waste at a rate of 3.2 times the weight of sulphur added to the pit. Between active periods of landfilling, a soil cover should be placed to minimize erosion and leachate production. At sites where groundwater might occasionally discharge through the sulphur waste pit, or when the physical properties of the cover soil might promote capillary rise of acidic water from the waste pit, a layer of limestone should be place on top of the sulphur waste to protect vegetative cover. A layer of limestone 25 cm thick should provide this protection. The final grade should be at least one metre above the top of the waste material and should prevent accumulation of surface water.

On-site pit burial must be conducted under an Environmental Protection and Enhancement Act approval, and groundwater quality monitoring must be undertaken to demonstrate no degradative environmental impact.

4 Approval Requirements

Disposal of sulphur contaminated solid wastes by landfilling is allowed according to the conditions and intent of this guide at any approved modified or sanitary landfill provided that permission is obtained from the landfill operator.

Disposal of sulphur contaminated solid wastes by on-site pit burial may be permitted according to the conditions and intent of this guide and as part of an Environmental Protection and Enhancement Act approval. Applications for on-site pit burial should be submitted to:

Alberta Environmental Protection
Air and Water Approvals Division
4th Floor, Oxbridge Place
9820 - 106 Street
Edmonton, Alberta
T5K 2J6

Disposal of sulphur contaminated solid wastes by land application are allowed according to the conditions and intent of this guide.

Documentation in support of soil remediation and treatment activities must be submitted to:

Alberta Environmental Protection
Chemicals Assessment and Management Division
5th Floor, Oxbridge Place
9820 - 106 Street
Edmonton, Alberta
T5K 2J6

Such documentation should demonstrate effective remediation in the case of cleaning up sulphur storage areas or accidental sulphur spills, or suitable treatment in the case of land application of sulphur containing wastes. Soil samples should be collected to at least the depth of contamination and be analyzed for pH, total sulphur, elemental sulphur, $CaCO_3$ equivalent, and other constituents, such as metals, that can impose an environmental impact with soil acidification. Documentation demonstrating no degradative impact on groundwater is also required for on-site pit burial of sulphur containing solid wastes.